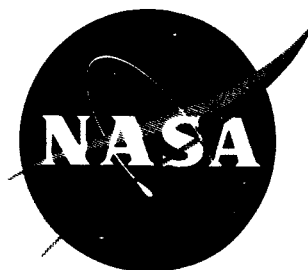


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TECHNICAL NOTE

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THE YIELD OF NITRIC OXIDE FROM PREMIXED FLAMES

OF HYDROGEN AND HYDROCARBONS

WITH NITROUS OXIDE

By Burton D. Fine and Albert Evans

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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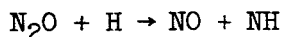
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OF HYDROGEN AND HYDROCARBONS
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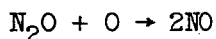
By Burton D. Fine and Albert Evans

SUMMARY

The yield of nitric oxide (NO) was measured downstream of rich flames of hydrogen (H₂) - nitrous oxide (N₂O) - nitrogen (N₂), H₂ - N₂O - carbon dioxide (CO₂), ethylene (C₂H₄) - N₂O - N₂, and acetylene (C₂H₂) - N₂O - N₂; lean H₂-N₂O flames with a nitrogen or argon diluent; and very lean H₂-N₂O flames on a cooled porous-plate burner. Results suggest that, in rich H₂-N₂O flames with an inert diluent, NO was formed by



whereas in rich hydrocarbon and H₂-N₂O-CO₂ flames the source of NO was

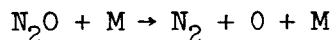


In rich H₂-N₂O-CO₂ flames, the concentration of oxygen atoms seemed to be greatly in excess of equilibrium. Results also suggested that the reaction



was unimportant in ethylene and acetylene flames.

Results for lean H₂-N₂O flames indicated that the thermal decomposition reaction



is relatively slow, even at very low equivalence ratios. Thus, the oxygen atom concentration in the flame is maintained primarily by equilibrium between oxygen atoms and molecules.

¹This paper was presented at the Western States Combustion Institute, San Diego, California, April 29-30, 1963. It is being released as a Technical Note by NASA to ensure its availability in published form.

INTRODUCTION

If a flame of hydrogen (H_2) with nitrous oxide (N_2O) is burned on a cooled porous-plate burner, nitric oxide (NO) is found in the burned gas just downstream of the flame. This is true for both rich and lean flames (refs. 1 and 2). The amount is small, of the order of a few mole percent, but exceeds the theoretical amount for complete equilibrium by many orders of magnitude. Lean of stoichiometric, the amount of NO in the burned gas increases slowly with distance because of oxidation of the excess N_2O , which proceeds, in part, by the reaction



Downstream of fuel-rich flames, on the other hand, the concentration of NO should decrease with distance because of reactions with reducing species and thermal decomposition. The orders of such reactions with respect to NO and their activation energies as well are, however, relatively high (refs. 3 and 4). Thus, it might be expected that, over large ranges of experimental conditions, the amount of NO produced would be sufficiently constant with distance that the yield of NO from a given flame could be characterized by a single value and determined by a very few sampling measurements. It might then be possible to correlate the NO yield data with initial and burned gas conditions in order to obtain information regarding chemical reactions taking place within the flame.

In a previous study (ref. 5), some NO yield values were reported for rich and lean H_2 - N_2O -diluent flames. Results rich of stoichiometric suggested that NO was formed by the reaction



since the NO yield was found to be roughly independent of initial equivalence ratio. Results for fuel-lean flames indicated proportionality between the NO yield and the concentration of oxygen atoms (O) in the burned gas, but little else in the way of detailed information was deduced.

In the present study, the NO yield measurements have been extended to include rich ethylene (C_2H_4) - N_2O and acetylene (C_2H_2) - N_2O flames with nitrogen (N_2) as a diluent at various pressures, burned gas temperatures, and initial equivalence ratios.² Additional data for H_2 flames have been obtained. These show the effects of CO_2 diluent for rich flames and of a large initial excess of N_2O for lean flames (initial equivalence ratios near 0.2). Also, more data have been obtained for lean flames with argon diluent. On the basis of these new data, the interpretation offered in the previous report (ref. 5) has been re-evaluated.

²Equivalence ratio is defined as the measured mole ratio n_{fuel}/n_{N_2O} divided by the mole ratio for a stoichiometric mixture. As used here, it does not retain its usual meaning entirely, since some of the N_2O present is removed by thermal decomposition and some of the initial mixtures contained added air.

EXPERIMENTAL PART

Apparatus and Procedure

A cooled porous-plate burner, 4 inches in diameter, was mounted in the base of a low-pressure chamber, as described previously (ref. 5). Sampling of the burned gas was done, as before, with quartz microprobes. The sampling zone extended downstream about 1 centimeter from the hot edge of the flame and was always isothermal within about 10° K. For rich flames the NO yield was defined as the average of up to four determinations through the sampling zone. For lean flames, the NO yield was taken to be the amount found about 1 centimeter downstream of the flame, at which position most of the N_2O that survived passage through the flame had been consumed.

Wherever possible, temperatures in the burned gas were determined with silica-coated platinum - platinum-13-percent-rhodium thermocouples, which were made by butt-welding wires 0.001 inch in diameter. All thermocouple readings were corrected for radiation by the procedure given in reference 6. For many $C_2H_2-N_2O-N_2$ flames, however, the burned gas temperatures were considerably higher than 2000° K, under which conditions the thermocouples failed. For such flames, it was necessary to estimate temperatures by a different method.

Reference 6 reports that the temperature dependence of the burning velocity of C_2H_4 -air flames on cooled porous-plate burners was about the same as for corresponding C_2H_2 -air flames. Therefore, it was assumed that a similar equality of temperature dependence held between $C_2H_4-N_2O-N_2$ and $C_2H_2-N_2O-N_2$ flames that contained similar proportions of diluent. First, the relation between temperature and burning velocity at pressures and equivalence ratios of interest was determined with thermocouples for the somewhat cooler ethylene flames. Then the temperatures for a few of the cooler acetylene flames were measured by thermocouple. Finally, the temperatures of the rest of the acetylene flames were estimated by assuming that the dependence of temperature on burning velocity, pressure, and equivalence ratio was the same for both fuels. Experimental checks with thermocouples showed that the temperature was insensitive to such changes in the proportion of diluent as were actually encountered. No correction was made, then, for such variation. Pressure was measured and controlled as previously described (ref. 5).

Gas analysis was done with a mass spectrometer, most species being analyzed directly. Water and, in some cases, carbon dioxide (CO_2) were trapped out in the sampling line and estimated by atom balance. For samples from very lean H_2-N_2O flames, which contained large amounts of both NO and O_2 , there was a small peak at mass 46 due to oxidation of a small part of the NO to NO_2 . At the beginning of a run, the 46 peak was absent, but it appeared shortly afterward and increased with time. Repetition of points at the beginning and end of a run established that the presence of the 46 peak did not measurably affect the very much larger 30 or 32 peaks. Downstream of rich hydrocarbon flames, a small amount of hydrocarbon was found, usually C_2H_2 , at a maximum mole fraction of about 0.001. This decayed rapidly with distance. A small peak was found at

mass 32, which represented the presence of either O_2 or OH in the burned gas, which likewise decayed rapidly. The other more important products, H_2 , CO , and NO , remained constant for residence times in the burned gas of several milliseconds; hence, for all rich flames, a single value served to characterize the NO yield.

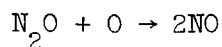
The range of experimental conditions covered was limited somewhat by problems of temperature measurement and pumping capacity, but mainly by flame stability problems. Thus, all rich hydrocarbon flames tended to be unstable at pressures much lower than 40 millimeters. For all rich flames, stability was not maintained if the equivalence ratio became too high. Rich flames of C_2H_2 and C_2H_4 with N_2O could not be maintained below 1850° or 1900° K, whereas corresponding H_2 flames remained stable down to almost 1500° K. Rather surprisingly, very lean H_2 - N_2O flames with no added diluent showed extraordinary stability down to equivalence ratios of less than 0.20. This may represent the fact that, under such conditions, the flame is supported, in part, by the exothermic decomposition of N_2O . At an equivalence ratio near 0.16, these flames developed a cellular structure and became unstable. Details of experimental conditions, along with the NO yield, are shown in table I for all new data.

Presentation of Results

All NO yield results, including those previously reported in reference 5, are shown in figures 1 to 3; yield is expressed as $n_{NO}/(n_{N_2O})_0$, the number of moles of NO produced per mole of N_2O fed into the flame, and is plotted against the reciprocal burned gas temperature in suitable correlating forms. The scatter of the data amounts to about ± 10 percent (occasionally greater) and can be accounted for in terms of temperature inconsistency ($\pm 25^\circ$ K), random errors of sampling and analysis (± 5 to ± 10 percent), and, as is discussed later, the empirical nature of the correlations. Furthermore, because of the approximate nature of the radiation correction, a consistent temperature error of about 50° K is likely. It should be noted that the NO yield values representing measurements reported in reference 5 are consistently 16 percent higher than the corresponding values given in this report. The difference represents a consistent error in reference 5 in the mass-spectrometer calibrations for NO and N_2O . The corrected rate expressions based on recalculation of the N_2O decay measurements of reference 5 are

$$k_1 = 4 \times 10^{10} e^{-\frac{24,000}{RT}} \quad (\text{liters}/(\text{mole})(\text{sec}))$$

(where R is the universal gas constant and T is temperature) which corresponds to the reaction



and

$$k_3 = 9 \times 10^{12} e^{-\frac{30,000}{RT}} \quad (\text{liters}/(\text{mole})(\text{sec}))$$

which corresponds approximately to the reaction



The level of the rate constants remains about the same as reported in reference 5, and all conclusions drawn on the basis of the earlier correlations remain valid.

RESULTS AND DISCUSSION

Rich Flames

Description of results. - Data for rich hydrogen flames are shown in figure 1. With nitrogen diluent, no significant effect of pressure or equivalence ratio is found. The yield of NO does increase with temperature at a rate corresponding to an energy of about 34 kilocalories per mole. An approximate value of the NO yield estimated from reference 2 is also shown and is in satisfactory agreement with present results. These data have already been presented and discussed in reference 5.

For the data with CO₂ diluent, it was found that part of the CO₂ initially present was converted to CO on passage through the flame. Thus, it appears that CO₂ acts in a manner more complicated than that of a simple diluent. In fact, a specific chemical effect is indicated, as shown by figure 1. Thus, the NO yield values are generally higher with CO₂ dilution than with N₂. There is a pressure effect. Most of the data were obtained for an equivalence ratio ϕ of 1.21; however, a few data points were obtained at other equivalence ratios. Examination of table I and figure 1 shows that there is an effect of equivalence ratio, the NO yield decreasing with increasing ϕ at constant pressure. Finally, the temperature dependence of the NO yield at constant pressure seems to be much less with CO₂ diluent than with N₂.

A satisfactory empirical correlation of the data with CO₂ dilution was found in terms of $\left[\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_0} \right] P^{1/2} (\phi - 1)^{1/2}$, where P is total pressure.

That function is shown plotted against the reciprocal temperature in figure 2. Its temperature dependence corresponds to about 8 kilocalories per mole.

It might be noted that analysis of the burned gas indicated that equilibrium among CO₂, H₂, CO, and H₂O was approximately attained. Thermodynamic calculations to this effect were supported by the observation that the concentration of neither CO nor H₂ showed any change with distance in the burned gas. Thus, there was no opportunity to measure a rate of approach to equilibrium,

as was done, for instance, in reference 7.

For hydrocarbon-N₂O-N₂ flames, the NO yield is roughly independent of pressure and primary fuel but decreases with initial equivalence ratio. A satisfactory empirical correlation was found between the product $\left[\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_0} \right] (\phi - 1)$ and reciprocal temperature. The change in NO yield with temperature was very nearly the same as for hydrogen-N₂O-N₂ flames. Results are shown in figure 3.

Discussion of results for hydrogen and hydrocarbon flames. - The fact that the NO yield changes regularly with burned gas temperature suggests that one (or both) of two types of process is important. First, a temperature-sensitive equilibrium involving NO may be established within and downstream of the flame. Second, reactions producing NO may compete with reactions decomposing N₂O, the effects of this competition on the change in NO yield with temperature representing the effects of differences in overall activation energies. For rich flames, it has not been possible to conceive of a reaction involving NO whose equilibration would begin to explain the results found. Thus, discussion of these results will be limited to consideration of the second type of process.

Proper interpretation of the results requires that all significant features of the data be explained in a mutually consistent fashion. For hydrocarbon flames, the results suggest rather unequivocally that NO is formed by reaction of N₂O with oxygen atoms, according to reaction (1). It is noted that the NO yield decreases markedly with increasing equivalence ratio, as would be expected if the formation of NO depended on the available concentration of oxygen atoms. Also, it is observed that the yield of NO from H₂ flames is considerably greater than the yield from the leanest of the hydrocarbon flames. This is consistent with the formation of NO by reaction (1), in all cases since unsaturated hydrocarbons react very much more rapidly with oxygen atoms than does H₂ (ref. 8).

On the other hand, certain apparent inconsistencies are found between the results for H₂ and for hydrocarbons. The fact that the NO yield from H₂ flames shows no systematic change with equivalence ratio suggests strongly that NO is formed by reaction of N₂O with H (reaction (2)) rather than reaction of N₂O with O (reaction (1)). This conclusion is further supported by the fact that the higher of two estimated values for the rate constant of reaction (1) (ref. 1) is about five times smaller than the rather well established rate constant for the reaction of H₂ with O (ref. 9). Thus, it might be concluded that NO is formed by different reactions in H₂-N₂O-N₂ and hydrocarbon-N₂O-N₂ flames. The fact that the temperature effect is similar for both types of fuel with N₂ diluent, however, seems to suggest that NO is formed by the same reaction in both cases.

These effects can be discussed more quantitatively if the results are analyzed in terms of the Zeldovich-Frank-Kametsky-Semenov theory (ref. 10) (subsequently referred to as the Semenov theory). Such a treatment would be similar to that used by Rozlovskii (ref. 11) in connection with the N₂O decomposition flame. With diffusion neglected, the nitric oxide yield may be written

$$\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_0} = \frac{1}{[\text{N}_2\text{O}]_0} \int \frac{d[\text{NO}]}{dt} \frac{dl}{v_0} \quad (4)$$

where t is time, dl is an increment of flame thickness, v_0 is the normal burning velocity of the unburned mixture, and the quantities in brackets are volume concentrations. Equation (4) can be integrated subject to the following assumptions:

(1) Chemical reaction takes place only at or very near the final burned gas temperature T_b . This assumption is a part of the Semenov theory.

(2) The rate of NO increase $d[\text{NO}]/dt$ is constant through the flame. This simplifying assumption is made in Rozlovskii's treatment (ref. 11).

(3) The limits of integration in equation (4) define the flame thickness l such that

$$(n_{\text{N}_2\text{O}})_0 = - \int_0^l d(n_{\text{N}_2\text{O}}) \quad (5)$$

Using these assumptions and integrating result in

$$\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_0} = \frac{1}{[\text{N}_2\text{O}]_0} \left(\frac{d[\text{NO}]}{dt} \right)^* \frac{l}{v_0} \quad (6)$$

where the starred derivative represents a constant, effective value for the flame. The quantity l/v_0 is proportional to a reaction time associated with the flame as a whole (ref. 12); therefore, the NO yield can be expressed as

$$\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_0} \propto \frac{1}{[\text{N}_2\text{O}]_0} \left(\frac{d[\text{NO}]}{dt} \right)^* \tau \quad (7)$$

It may be assumed that τ is the reaction time associated with the reaction



which, in the absence of NO formation, would account for all the N_2O decay through the flame (ref. 2). For rich flames

$$\tau^{-1} = \frac{d \ln [\text{N}_2\text{O}]}{dt}^*$$

The predicted behavior of equation (7) may now be compared depending on

whether reaction (1) or (2) is assumed as the source of NO. It should be noted that both reactions predict directly that the NO yield should be independent of pressure. Thus, $[N_2O]_0 \propto P$, where P is total pressure. Since both reactions (1) and (2) are second order, $(d[NO]/dt)^* \propto P^2$ in either case. Finally, since the overall reaction (8) is second order, $\tau \propto P^{-1}$ (ref. 13). Thus, an overall zero pressure dependence is predicted, as was observed.

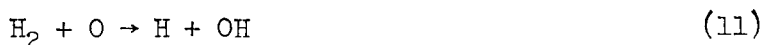
With regard to the effect of equivalence ratio, the situation is more complicated. It may first be assumed that NO is formed by reaction (1), in which case

$$\left(\frac{d[NO]}{dt}\right)^* = k_1[N_2O]^*[O]^* \quad (9)$$

If the oxygen atoms are assumed to be in a steady state, being formed by



(where M is any species present) and destroyed by reactions (1), (3), and



the equation

$$\left(\frac{d[NO]}{dt}\right)^* = \frac{k_1 k_{10} ([N_2O]^*)^2 [O]^*}{(k_1 + k_3)[N_2O]^* + k_{11}[H_2]^*} \quad (12)$$

is obtained, where all starred quantities are effective values in the flame zone. The value of k_{11} is well known (ref. 9). When expressions for k_1 and k_3 mentioned previously are used (that is, a value of k_1 obtained from flame sampling measurements), it can be seen that $(k_1 + k_3)$ and k_{11} are about

in the ratio 6:1. Thus, if $[N_2O]^*$ and $[H_2]^*$ are not too different (that is, the range of equivalence ratios is not too large), $d[NO]^*/dt$ will depend only weakly on hydrogen concentration, and, from the Semenov theory,

$(1/[N_2O]_0)(d[NO]/dt)^*$ will be similarly independent of equivalence ratio.

It is easily shown, however, that, if the main source of heat production in the flame is reaction (8), $\tau \propto ([H]^*)^{-1}$. The variation of $[H]^*$ with equivalence ratio is not precisely known. Nevertheless, it is quite unlikely that $[H]^*$ is independent of ϕ . Thus, it is predicted that the NO yield depends on ϕ . It should be noted that, if a steady state is not assumed for oxygen atoms, an even stronger dependence of NO yield on ϕ is predicted. On the other hand, if it is assumed that NO is formed by reaction (2),

$$\left(\frac{d[NO]}{dt}\right)^* = k_2[N_2O]^*[H]^* \quad (13)$$

In this case, it is seen that the NO yield does not depend on ϕ , as is observed. Thus, as concluded intuitively in reference 5, the equivalence ratio effect favors reaction (2) over reaction (1).

The results with CO_2 dilution suggest that, while much of the CO_2 that reacts in the flame does so by way of the reaction



an important fraction ultimately undergoes thermal dissociation to give oxygen atoms. The oxygen atoms are formed in a sufficient quantity that the main reaction forming NO becomes reaction (1) instead of (2). A simple equilibrium calculation shows that oxygen atoms must exceed their equilibrium concentration by many orders of magnitude to have a noticeable effect on the NO yield. Thus, the actual mechanism of oxygen atom formation is almost certainly quite complicated.

The mechanism proposed for NO formation in rich $\text{H}_2\text{-N}_2\text{O-CO}_2$ flames is obviously consistent with the observed effect of equivalence ratio. It is also consistent with the pressure effect since, for a nonequilibrium system, the concentration of active species can increase strongly with decreasing pressure. Finally, comparison of temperature effects shows that the main reaction forming NO with N_2 dilution is not the same as with CO_2 dilution. As will be shown later, a relatively small rate of increase of NO yield with temperature is characteristic of situations where NO is formed in H_2 flames by reaction (1). Thus, results with CO_2 corroborate the idea that, with an inert diluent, NO in rich $\text{H}_2\text{-N}_2\text{O}$ flames is formed by reaction (2). It can be concluded, then, that the similarity in temperature effects between NO yield data from $\text{H}_2\text{-N}_2\text{O-N}_2$ and hydrocarbon- $\text{N}_2\text{O-N}_2$ flames is, in fact, coincidental and that the reactions mainly responsible for NO formation are different in hydrogen and hydrocarbon flames.

Further discussion of nitric oxide yield results from hydrocarbon flames. - As noted previously, the NO yield from C_2H_4 and C_2H_2 flames decreased strongly with increasing equivalence ratio. This seems to indicate that NO is formed almost exclusively by reaction (1). Then, since reaction (2) ($\text{N}_2\text{O} + \text{H} \rightarrow \text{NO} + \text{NH}$) must be unimportant, reaction (8) ($\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH}$), which occurs in parallel with reaction (2), is also unimportant. Further evidence that reaction (8) does not contribute much to N_2O decay is offered by comparison of data for C_2H_2 and C_2H_4 flames. Thus, it was found that the mole fraction of H_2 in the burned gas from ethylene flames was more than twice as great as from acetylene flames. The NO yield data for the two fuels roughly coincided, however. It seems reasonable to expect that the hydrogen atom concentration in the flame should vary directly with the amount of H_2 in the burned gas. By definition, the NO yield represents the number of moles of NO formed per mole of N_2O consumed. Thus, it can be inferred that the rate of N_2O consumption in the flame was not measurably affected by a change in hydrogen atom concentration corresponding to

the observed change in H_2 level in the burned gas. This seems to indicate that reaction (8) is unimportant in hydrocarbon- N_2O flames. The simplest likely path for N_2O consumption would seem to be reactions of the type



where R is a monovalent hydrocarbon radical. If reaction (15) is important in the presence of even a relatively small concentration of hydrogen atoms, its activation energy cannot be much higher than that of reaction (8). Thus, consumption of hydrocarbon by the sequence of reactions



is probably not important since reaction (10) involves an activation energy of 59 kilocalories at low pressures.

Further evidence may be offered to support the idea that, in rich hydrocarbon- N_2O flames, the concentration of hydrogen atoms is actually negligibly small (from the standpoint of flame reaction rates) compared with H_2 - N_2O flames. Thus, in the investigation of reference 14, it was found that, downstream of rich H_2 - O_2 -diluent flames, the concentration of hydrogen atoms exceeded equilibrium by several orders of magnitude. Downstream of corresponding hydrocarbon flames, however, the concentration of hydrogen atoms found was the equilibrium value, within experimental error.

Lean Flames

Description of results. - The new NO yield data for H_2 - N_2O diluent flames are shown in figure 3 along with the data previously presented in reference 5, which have been corrected, as discussed above. It can be seen from figure 3 and table I that all yield values at constant pressure are correlated with the square root of the downstream oxygen concentration for an overall variation in oxygen concentration of about a factor of 10. As noted previously, the levels of NO concentration are generally much higher than for rich flames. The correlating yield function increases substantially with decreasing pressure, the change in NO yield itself with pressure being in the same direction, but much smaller. A point computed from recent sampling data of reference 9 for an H_2 - N_2O -air flame at a pressure of 20 millimeters is in reasonable agreement. The temperature dependence of the NO yield is independent of pressure, diluent, and oxygen concentration. It amounts to about 14 kilocalories, a value substantially less than for rich flames with an inert diluent, but only slightly greater than the value found for rich H_2 - N_2O - CO_2 flames.

Discussion of results. - The correlation with oxygen concentration, even for the very lean flames, suggests that, in a general way, the NO yield is proportional to the oxygen atom concentration in the flame.

In lean flames, there are two possible sources of oxygen atoms, reaction (10) ($\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O} + \text{M}$) and reversible dissociation of oxygen molecules



produced by reaction (3) ($\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2 + \text{O}_2$). The nature of the correlation observed suggests that the contribution of reaction (10) is small. If it is assumed that in the part of the flame where NO is produced the change in concentration of oxygen atoms with distance is small, and if reaction (17) is at or near equilibrium,

$$[\text{O}] = K[\text{O}_2]^{1/2} \quad (18)$$

where K is a constant. Actually, strong evidence exists (refs. 1 and 5) that, downstream of lean H_2 - N_2O -diluent flames, the concentration of oxygen atoms is in great excess of equilibrium, so that K is probably not a true equilibrium constant. Thus, equation (17) represents the overall result of a complex process, analogous to the dissociation of CO_2 to produce oxygen atoms, which was discussed earlier in connection with rich H_2 - N_2O - CO_2 flames.

The rate of formation of NO in the flame by reaction (1) can be written as

$$\left(\frac{d[\text{NO}]}{dt}\right)^* = 2k_1K([\text{O}_2]^*)^{1/2}[\text{N}_2\text{O}]^* \quad (19)$$

since reaction (2) is not likely to be important in lean flames. If $[\text{O}_2]^*$ equals the value measured downstream of the flame,

$$[\text{O}_2]^{-1/2} \frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_0} = \frac{2}{[\text{N}_2\text{O}]_0} \int k_1K[\text{N}_2\text{O}]^* \frac{dl}{v_0} \quad (20)$$

This equation is analogous to equation (4) for rich flames. By the same kind of argument as was used for rich flames, it can be shown that, for lean flames,

$[\text{O}_2]^{-1/2} n_{\text{NO}} / (n_{\text{N}_2\text{O}})_0$ will vary inversely with pressure. This is fairly close

to what is observed. Equation (20) might also be used to predict the observed fact that the temperature dependence of the NO yield is independent of equivalence ratio over a very wide range. A difficulty arises, however, since, for very lean flames, reaction (3) may contribute significantly to heat release through the flame as well as reaction (8) ($\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH}$). Thus, in order to explain the result, it must be concluded either that reaction (8) continues to determine the flame properties at very lean equivalence ratios or that the activation energy for reaction (3), which would be important in very lean flames, is not very different from that for reaction (8). In either case, the activation energy of the controlling reaction would vary slightly, at most, with change in equivalence ratio. The latter of the two possibilities is con-

sistent with conclusions reached in reference 5, regarding the true values of E_3 and E_1 , but, in view of the complicated nature of the flame reactions, the first possibility cannot be excluded.

The fact that the temperature dependence on the NO yield is so very different for lean and rich flames with inert diluents suggests examination of the possibility that, downstream of lean flames, NO is maintained by an equilibrium of some sort. The most likely possibility would be



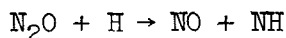
This equilibrium is consistent with the dependence of NO yield on $[\text{O}_2]^{1/2}$ that is observed. Equilibration of reaction (21) predicts that the NO yield function will vary with pressure as $P^{-1/2}$ and will show a change with temperature corresponding to 22 kilocalories. This is not too different from what is observed. The observed concentration product for reaction (21) is, however, greater than 10^{-1} near 1800°K , whereas the value of the equilibrium constant is about 10^{-2} . Furthermore, with argon as the diluent, it is possible to vary the N_2 concentration in the burned gas by a factor of just over 2.5. In spite of the large scatter of the data, the effect of this change should be apparent if reaction (21) is equilibrated. Actually, no significant effect is found. Thus, it seems fairly certain that the equilibrium is not maintained.

In general, it can be concluded that, for lean flames as well as rich, examination of the NO yield over a range of experimental cases gives some information on chemical processes within the flame.

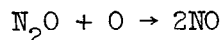
SUMMARY OF RESULTS

The nitric oxide (NO) yield was measured from lean and rich premixed flames of hydrogen, ethylene, and acetylene on a cooled porous burner. Various diluents were used. The following results were obtained:

1. The variation of NO yield with equivalence ratio suggested that in hydrogen (H_2) - nitrous oxide (N_2O) flames with inert diluents NO was formed by the reaction

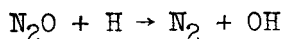


whereas in corresponding hydrocarbon- N_2O -nitrogen and hydrogen - N_2O - carbon dioxide flames NO was formed mainly by



2. The addition of carbon dioxide to a rich H_2 - N_2O mixture gave a flame in which oxygen atoms appeared to exceed their equilibrium concentration by many orders of magnitude.

3. Since the NO yield from ethylene flames was the same as from corresponding acetylene flames, it appears that the reaction



is unimportant in hydrocarbon-N₂O flames, and that N₂O decay takes place through reaction of N₂O with monovalent hydrocarbon radicals.

4. The variation of NO yield with pressure, oxygen concentration, and initial equivalence ratio for lean H₂-N₂O-diluent flames indicated that the contribution of thermal decomposition of N₂O to the overall flame reaction was small.

Lewis Research Center

National Aeronautics and Space Administration

Cleveland, Ohio, February 15, 1963

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TABLE I. - NITRIC OXIDE YIELD DATA

(a) Rich hydrocarbon - nitrous oxide - nitrogen flames

Fuel	Pressure, P, mm Hg	Burned gas tempera- ture, T_o , °K	Initial burning velocity, v_o , cm/sec	Equiva- lence ratio, ϕ	Initial diluent- fuel ratio, $\left(\frac{n_{dil}}{n_{fuel}}\right)_o$	Nitric oxide yield function, $\frac{n_{NO}}{(n_{N_2O})_o}$ ($\phi - 1$)	
Ethyl- ene	44	2090	23.8	1.12	4.83	0.0031	
		2085	25.1	1.41	4.45	.0028	
		2085	25.3	1.51	4.02	.0032	
		2080	30.4	1.33	4.65	.0043	
		2020	25.2	1.32	4.65	.0034	
	88	2060	18.7	1.33	4.65	0.0030	
		2000	15.2	1.33	4.65	.0025	
		1995	12.5	1.51	4.02	.0025	
		1980	12.6	1.51	4.09	.0026	
		1950	13.0	1.12	5.00	.0025	
		1940	12.6	1.32	4.65	.0023	
		1920	10.7	1.12	5.00	.0013	
		Acety- lene	44	2230	27.8	1.29	5.12
	2220			23.1	1.54	5.15	.0068
2215	27.2			1.43	4.85	.0062	
2180	24.6			1.16	4.41	.0055	
2170	24.7			1.29	5.15	.0070	
2140	21.4			1.16	4.35	.0054	
2080	19.3			1.32	5.30	.0054	
88	2050			13.9	1.29	5.12	0.0042
	2010		13.6	1.43	4.85	.0030	
	2000		12.3	1.29	5.15	.0032	

TABLE I. - Continued. NITRIC OXIDE YIELD DATA

(b) Rich hydrogen - nitrous oxide - carbon dioxide flames

Pressure, P, mm Hg	Burned gas tempera- ture, T, °K	Initial burning velocity, v _o , cm/sec	Initial fuel - nitrous oxide ratio, $\left(\frac{n_{\text{fuel}}}{n_{\text{N}_2\text{O}}}\right)_o$	Initial diluent- fuel ratio, $\left(\frac{n_{\text{dil}}}{n_{\text{fuel}}}\right)_o$	Nitric oxide yield function, $\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_o} P^{1/2} (\phi - 1)^{1/2},$ atm ^{1/2}
27	1800	57.8	1.21	0.97	0.00317
	1740	48.5	↓	↓	.00305
	1640	33.3	↓	↓	.00232
	1690	40.8	↓	↓	.00293
44	1760	35.5	1.21	1.54	0.00318
	1740	39.0	↓	.97	.00329
	1705	27.0	↓	.77	.00278
	1640	25.0	↓	.97	.00293
	1718	29.8	↓	.97	.00341
	1632	29.0	1.43	.82	.00294
	1700	28.2	1.10	1.06	.00292
	1773	34.3	1.10	1.06	.00368
	1575	20.4	1.21	.97	.00263
	1570	27.9	1.44	.82	.00248
88	1675	21.6	1.21	1.54	0.00326
	1665	17.8	↓	.97	.00248
	1590	14.9	↓	.97	.0273
	1585	13.5	↓	.97	.0294

TABLE I. - Concluded. NITRIC OXIDE YIELD DATA

(c) Lean hydrogen - nitrous oxide flames

Pressure, P, mm Hg	Diluent	Temperature, T, °K	Initial burning velocity, v _o , cm/sec	Initial fuel- nitrous oxide ratio, $\left(\frac{n_{\text{fuel}}}{n_{\text{N}_2\text{O}}}\right)_o$	Initial diluent- fuel - ratio, $\left(\frac{n_{\text{dil}}}{n_{\text{fuel}}}\right)_o$	Nitric oxide yield, $\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_o}$	Nitric oxide yield function, $\frac{n_{\text{NO}}}{(n_{\text{N}_2\text{O}})_o} [\text{O}_2]^{-1/2},$ (liters/mole) ^{1/2}	Mole fraction of oxygen
44	None	1867	23.4	0.198	0	0.155	19.4	0.175
88	Argon	1980 1870 1780	27.4 20.4 17.1	0.714 .714 .714	2.00 2.00 2.00	0.071 .065 .057	15.9 14.3 9.1	0.026 .029 .027
90	None	1934 1888 1875 1867 1829 1780	17.2 16.7 13.8 23.4 14.5 9.67	0.167 .192 .192 .198 .253 .253	0 ↓	0.164 .136 .120 .155 .119 .109	13.9 11.4 11.3 13.3 10.1 9.2	0.187 .184 .189 .175 .175 .177
210	None	1797 1751	7.14 6.25	0.192 .253	0 0	0.115 .103	6.1 5.7	0.190 .175

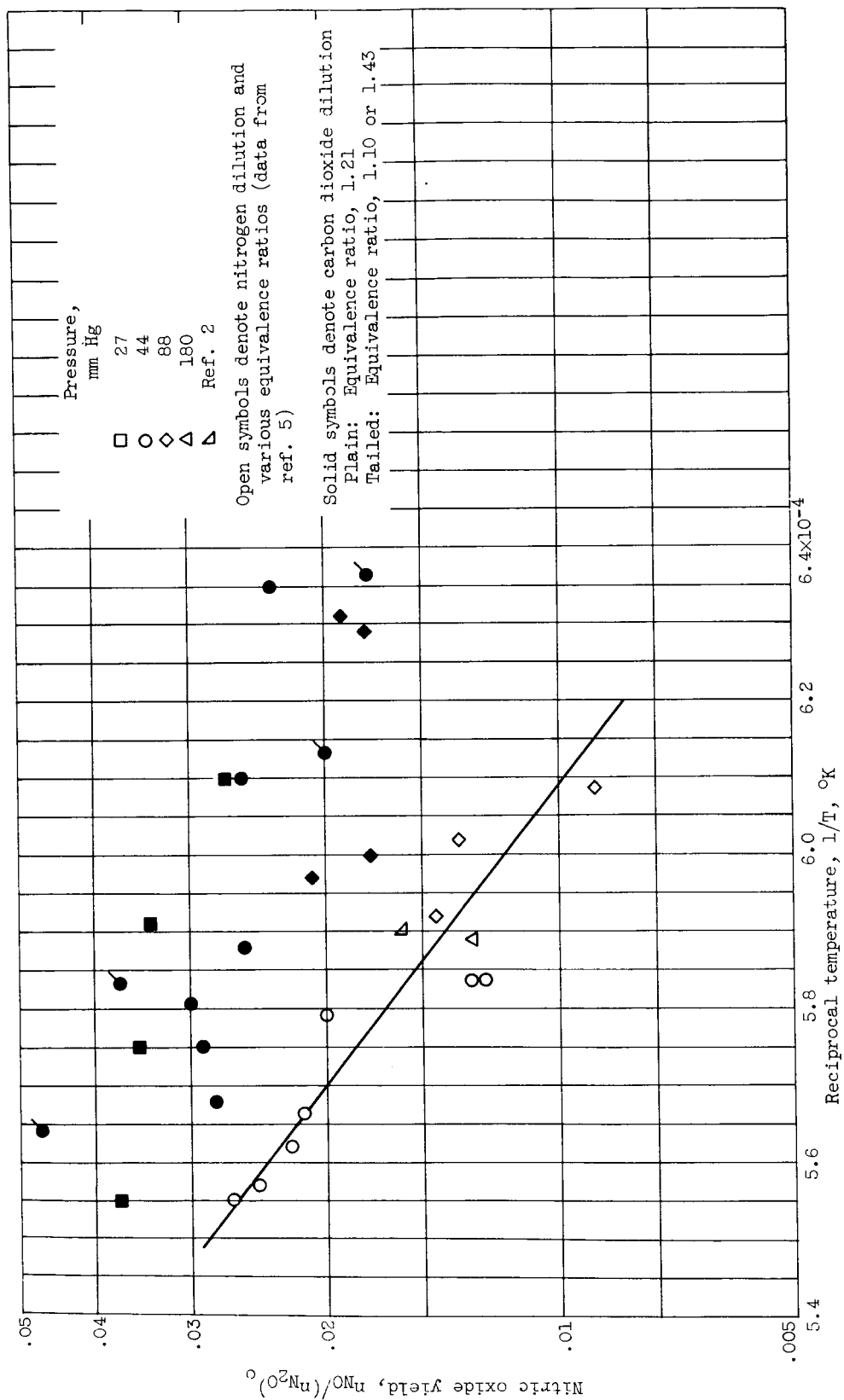


Figure 1. - Nitric oxide yield from rich hydrogen - nitrous oxide - diluent flames.

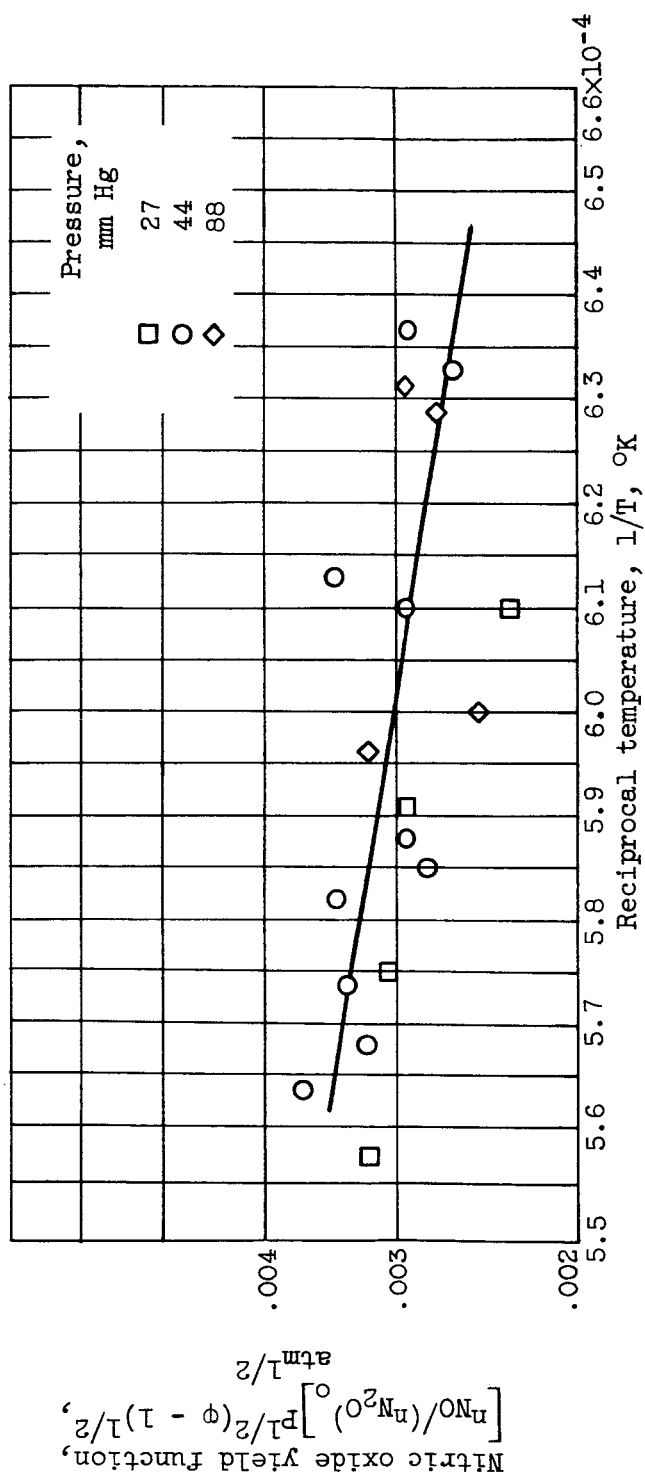


Figure 2. - Correlation of nitric oxide yield for rich hydrogen - nitrous oxide - carbon dioxide flames.

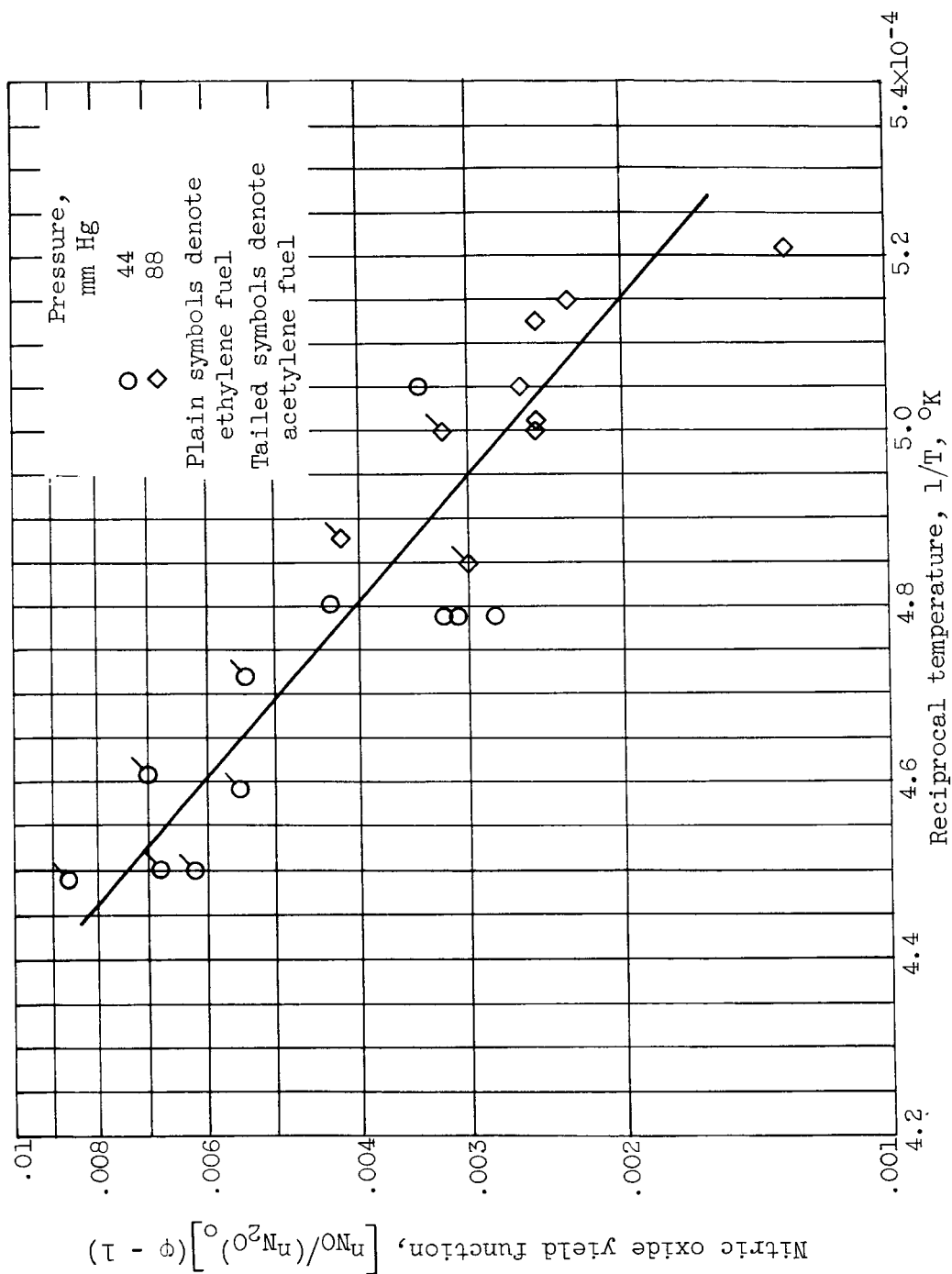


Figure 3. - Nitric oxide yield from rich acetylene - nitrous oxide - nitrogen and ethylene - nitrous oxide - nitrogen flames. Initial fuel - nitrous oxide equivalence ratios range from about 1.1 to 1.5.

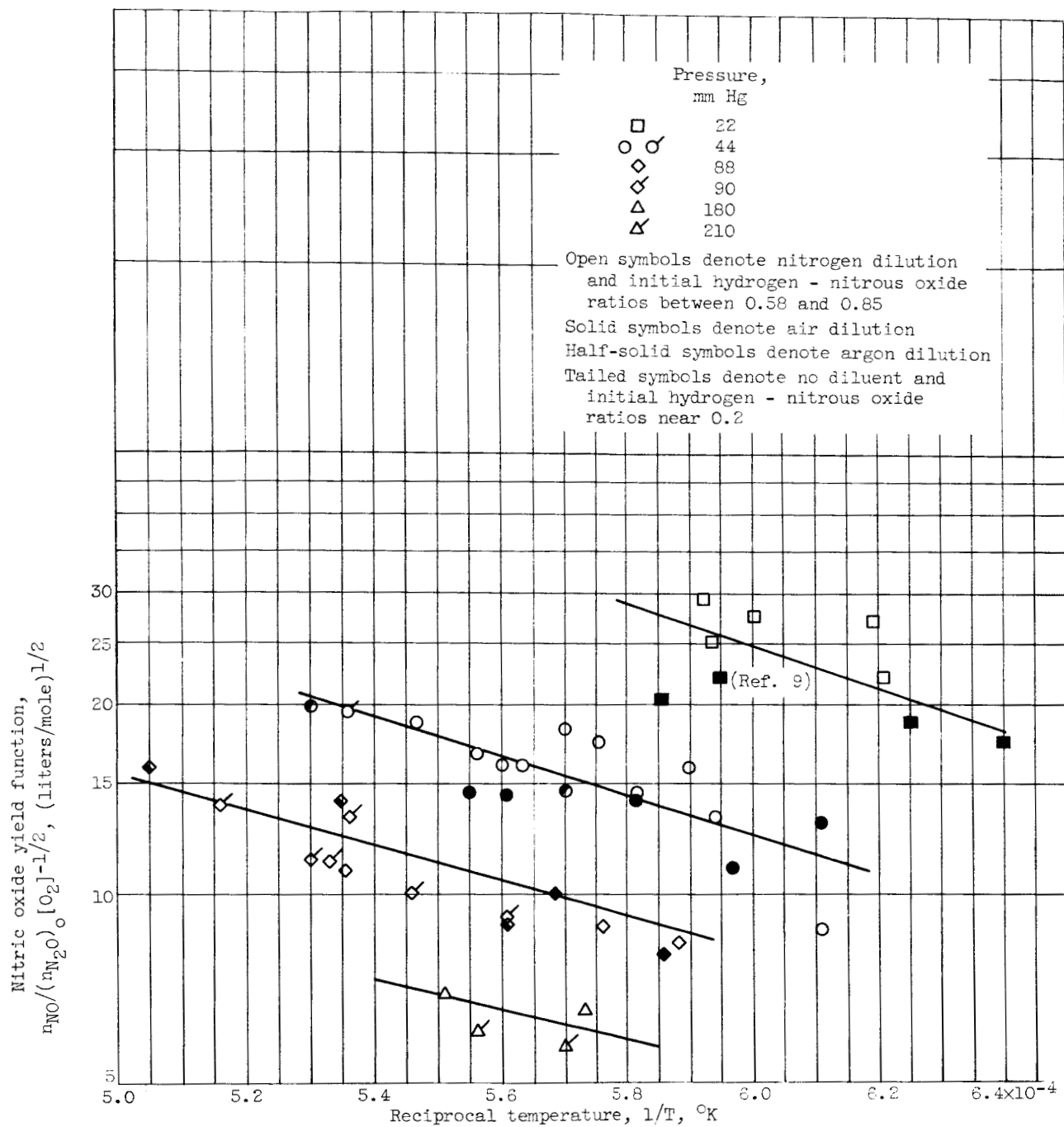


Figure 4. - Nitric oxide yield from lean hydrogen - nitrous oxide - diluent flames.